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(71) Applicant (for all designated States except US): **UNIVERSITY COLLEGE CARDIFF CONSULTANTS LIMITED** [GB/GB]; 30-36 Newport Road, Cardiff, South Glamorgan, CF24 ODE (GB).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **HUTCHINGS, Graham John** [GB/GB]; Rocklands, Symonds Yat, Ross on Wye, Hereford & Worcester, HR9 6DY (GB). **NTAINJUA, Edwin Ndifor** [GB/GB]; 21 Gabalfa Avenue, Llandaff North, Cardiff, CF14 2SG (GB).

(74) Agents: **HASLAM, Simon, David** et al.; Abel & Imray, 20 Red Lion Street, London WC1R 4PQ (GB).

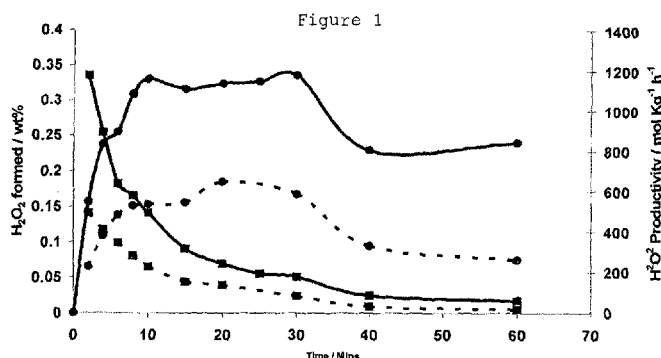
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(54) Title: CATALYST COMPOSITIONS, METHOD OF MAKING THE SAME AND METHODS OF MAKING HYDROGEN PEROXIDE



(57) Abstract: A method of producing hydrogen peroxide is provided, in which hydrogen and oxygen are contacted with a catalyst composition comprising a heteropolyacid support and gold. A method of treating polluted water is also provided, as is a catalyst useful in the methods of producing hydrogen peroxide and treating polluted water.

**Catalyst compositions, method of making the same and methods
of making hydrogen peroxide**

The present invention relates to catalyst compositions, methods of making said catalyst compositions and the use of catalyst compositions to make hydrogen peroxide.

The production of hydrogen peroxide from hydrogen and oxygen typically involves the reaction of hydrogen and oxygen in the presence of a catalyst at a low temperature (typically 2°C) and in a solvent comprising water mixed with a co-solvent, such as an alcohol. Whilst this method is effective, operating at low temperatures usually requires cooling, which is expensive and uses energy. Furthermore, the proportion of alcohol used is typically quite high (typically about the same volume as the amount of water used), which is generally undesirable, because it is generally undesirable to use organic solvents, such as organic alcohols.

WO2007/007075 discloses catalysts for promoting the production of hydrogen peroxide from oxygen and hydrogen. The catalysts of the prior art comprise gold, palladium or gold and palladium supported on various acid-washed supports, such as zeolites, titania, silica and activated carbon.

Whilst these catalysts have been found to be effective under certain conditions, these known catalysts have been found to be not terribly effective in water alone or at elevated temperatures.

The catalyst compositions of the present invention mitigate against one or more of the problems mentioned above.

In accordance with a first aspect of the present invention, there is provided a catalyst composition comprising a heteropolyacid support and gold.

The catalyst composition preferably further comprises palladium.

The catalyst composition of the first aspect of the present invention has been found to be surprisingly good at catalysing the production of hydrogen peroxide from oxygen and hydrogen in water and, in certain cases, to be particularly good at catalysing said reaction at temperatures which are higher than those conventionally used and in water (in the absence of a substantial amount of co-solvent, such as alcohol), especially when the catalyst composition comprises gold and palladium.

Heteropolyacid supports are well known to those skilled in the art but are described here. A heteropolyacid comprises:

One or more addenda atoms (typically a metal and usually a Group 5 or 6 transition metal, such as tungsten, vanadium or molybdenum, although other metals may be used, such as titanium and iron);

oxygen;

one or more hetero atoms (typically an element from the p-block of the periodic table, such as silicon, phosphorous or arsenic, although other atoms, such as aluminium and tellurium may be used);

and acidic hydrogen atoms.

Heteropolyacids include those comprising anions having a Keggin structure, a Dawson structure, a Lindqvist structure and an Anderson structure.

Those skilled in the art will realise that structural or chemical variations of the classical structures mentioned above (such as Keggin, Dawson, Lindqvist and Anderson) are permitted. For example, one or more of the oxygen atoms in

the support may be substituted by a different element e.g. S or Br. A heteropolyacid having a so-called lacunary structure may be used (a lacunary structure is one in which one or more of the addenda atoms and associated oxide ions is absent from the heteropolyacid).

It is preferred that the heteropolyacid support is insoluble in water. This may be achieved, for example, if the heteropolyacid support is in the form of a salt, for example, a salt of a metal (e.g. caesium, cerium or rubidium) or ammonium.

The catalyst composition may comprise at least one further catalytic metal in addition to gold and palladium (if present). For example, the catalyst composition may comprise one or more of platinum, copper, tin, nickel, ruthenium and rhenium

It is preferred that gold (and preferably palladium, if present) is distributed (and preferably uniformly distributed) throughout the catalyst composition. This may be achieved, for example, by providing the gold (and palladium if present) in ion-exchanged form.

It is preferred that the catalyst composition comprises gold and palladium, and that the gold and palladium are distributed throughout the catalyst composition.

Alternatively or additionally, gold (and optionally palladium) may be provided as particles present on the surface of the heteropolyacid support. This is generally known in the art as the metal being "supported" by the catalyst.

The catalyst composition may therefore comprise gold (and optionally palladium) distributed throughout the catalyst composition and/or gold (and optionally palladium) provided as

particles present on the surface of the support. It is generally preferred, however, that the gold (and palladium, if present) will either be distributed throughout the catalyst composition or be provided as particles present on the surface of the support.

The catalyst composition may comprise a further support in addition to the heteropolyacid support. The further support may, for example, comprise TiO_2 .

If the catalyst composition comprises gold (and palladium, if present) distributed throughout the catalytic composition, the catalyst composition may typically comprise 0.1 to 5 wt% gold and palladium, optionally from 0.1 to 3 wt% gold and palladium and further optionally from 0.1 to 1 wt% gold and palladium. The percentage figures above relate to the total weight of gold and palladium distributed throughout the catalyst composition as a percentage of the total weight of the catalyst composition. In one embodiment, the percentages above are optionally preferred if there is no further support in the catalyst composition. In the event that the catalyst composition comprises a further support, the catalyst composition may typically comprise 0.05 to 3 wt% gold and palladium, optionally from 0.05 to 1.5 wt% gold and palladium and further optionally from 0.05 to 0.5 wt% gold and palladium.

If the catalyst composition comprises gold (and palladium, if present) provided as particles present on the surface of the heteropolyacid support, the catalyst composition typically comprises from 0.5 to 10wt% gold and palladium, optionally comprises from 1 to 6wt% gold and palladium, and further optionally comprises from 3 to 5wt% gold and palladium. The percentage figures above relate to the total weight of gold and palladium provided as particles present on the surface of

the heteropolyacid support as a percentage of the total weight of the catalyst composition. In one embodiment, the percentages above are optionally preferred if there is no further support in the catalyst composition. In the event that the catalyst composition comprises a further support, the catalyst composition typically comprises from 0.25 to 5wt% gold and palladium, optionally comprises from 0.5 to 3wt% gold and palladium, and further optionally comprises from 1.5 to 2.5wt% gold and palladium.

If the catalyst composition comprises gold and palladium, the molar ratio of palladium:gold may typically be in the range from 0.1:1 to 10:1, optionally in the range from 0.2:1 to 5:1, further optionally in the range from 0.2:1 to 5:1, further more optionally in the range from 1:1 to 3:1 and alternatively in the range from 1.4:1 to 3:1.

In accordance with a second aspect of the present invention, there is provided a method of making a heteropolyacid catalyst composition comprising gold (and optionally palladium), said method comprising:

- (i) Generating a heteropolyacid support;
- (ii) Depositing a gold salt (and optionally a palladium salt) onto the heteropolyacid support to form a catalyst precursor;
- (iii) Calcining the catalyst precursor to form a heteropolyacid catalyst composition.

Step (i) preferably comprises generating a solid support.

Step (i) may comprise generating a heteropolyacid support precursor and subsequently calcining said heteropolyacid support precursor to form the heteropolyacid support.

Calcining may be omitted from step (i), and so step (ii) may comprise depositing a gold salt (and optionally a palladium salt) onto a non-calcined heteropolyacid support.

In accordance with a third aspect of the present invention, there is provided a method of making a heteropolyacid catalyst composition comprising gold (and optionally palladium), said method comprising:

- (i) Reacting a gold salt (and optionally a palladium salt) with an acid to form a catalyst precursor;
- (ii) Calcining the catalyst precursor to form a heteropolyacid catalyst composition.

The acid may be, for example, tungstophosphoric acid ($\text{H}_3\text{PW}_{12}\text{O}_{40}$).

The methods of the second and third aspects of the present invention may be used to make the catalyst composition of the first aspect of the present invention.

In accordance with a fourth aspect of the present invention, there is provided a method of producing hydrogen peroxide in which hydrogen and oxygen are contacted with a catalyst composition according to the first aspect of the present invention.

The method may take place at a temperature in the range of from 0°C to 50°C. Whilst the reaction proceeds more effectively at lower temperatures, for example, at 2-5°C, the catalyst compositions of the first aspect of the present invention are more effective than many known catalyst compositions at temperatures higher than 2-5°C (for example, at 15-25°C). It is therefore preferred that the method takes place at a

temperature of at least 10°C, preferably at least 15°C and further more preferably in the range from 15°C to 25°C.

A method typically takes place in a reaction medium.

The liquid component of the reaction medium is typically aqueous. Whilst the reaction proceeds more effectively when the liquid component of the reaction medium comprises water and a substantial proportion (e.g. 50% by volume) of a co-solvent (typically an alcohol), the catalysts of the first aspect of the present invention have proved to be unexpectedly effective when the solvent was substantially water alone. It is therefore preferred that the liquid component of the reaction medium is typically at least 60wt% water, optionally at least 90wt% water and further optionally substantially only water.

In accordance with a fifth aspect of the present invention, there is provided a method of treating polluted water with hydrogen peroxide, said method comprising generating hydrogen peroxide using a catalyst composition.

The catalyst composition may comprise one or more reactive metals. The reactive metals may be one or more of gold, palladium, platinum, tin, ruthenium and rhodium. The catalyst composition may optionally comprise gold, and may further additionally comprise one or more of palladium, platinum, tin, ruthenium and rhodium.

The catalyst composition may comprise a support. The support may comprise one or more of heteropolyacid, TiO_2 , SiO_2 , CeO_2 , ZrO_2 , carbon, Al_2O_3 , Fe_2O_3 , MgO and a zeolite. The support may optionally comprise a heteropolyacid, and may further additionally comprise one or more of palladium, platinum, tin, ruthenium and rhodium.

The catalyst composition may comprise a catalyst composition according to the first aspect of the present invention.

The hydrogen peroxide may be generated by contacting hydrogen and oxygen with the catalyst composition.

The method of treating polluted water may comprise generating hydrogen peroxide upstream of the polluted water. For example, hydrogen peroxide may be generated in clean water which is then admixed with the polluted water.

The temperature of the polluted water may optionally be up to 50°C.

The present invention will now be described by way of example only with reference to Figure 1 which shows the wt% of hydrogen peroxide formed and the hydrogen peroxide productivity as a function of reaction time for an example of a catalyst in accordance with the present invention and for a comparative catalyst.

The manufacture of several examples of catalyst compositions in accordance with the present invention is now described.

Catalyst Composition 1 - $\text{Pd}_{0.1}\text{Au}_{0.033}\text{Cs}_{2.5}\text{H}_{0.2}\text{PW}_{12}\text{O}_{40}$

One example of catalyst in accordance with the first aspect of the present invention in which the gold and palladium are distributed throughout the catalyst composition was made as follows. Aqueous solutions of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (Johnson Matthey) and $\text{Pd}(\text{NO}_3)_2$ (Sigma Aldrich, UK) were added drop-wise to a solution of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (Sigma Aldrich, UK), and the resulting reaction mixture was stirred for 5 minutes. CsNO_3 was then added in a drop-wise manner. The resulting solution was continuously stirred while heating at 60 °C for 12 h to obtain a solid product which was then dried overnight at 70 °C, followed by calcination at 300 °C for 2 h to form the final catalyst. For

the preparation of 1 g of this catalyst composition the following aqueous solutions were used: $\text{H}_3\text{PW}_{12}\text{O}_{40}$ solution (3 ml, 0.8926 g in 3 ml), Au solution (0.1660 ml, 12.25 g Au in 1000 ml), $\text{Pd}(\text{NO}_3)_2$ (2 ml, 0.0071 g in 2ml) and CsNO_3 (2 ml, 0.1510 g in 2ml). The amount of each starting material ($\text{H}_3\text{PW}_{12}\text{O}_{40}$, Au solution (12.25 g in 1000 ml, $\text{Pd}(\text{NO}_3)_2$, or CsNO_3) dissolved or added was varied to form other catalysts compositions.

Catalyst Composition 2 - $\text{Pd}_{0.075}\text{Au}_{0.05}\text{Cs}_{2.5}\text{H}_{0.2}\text{PW}_{12}\text{O}_{40}$

A further example of a catalyst composition in accordance with the present invention was made substantially as described above with reference to Catalyst Composition 1. To prepare 1 g of this catalyst composition the following aqueous solutions were used: $\text{H}_3\text{PW}_{12}\text{O}_{40}$ solution (3 ml, 0.8924 g in 3 ml), Au solution (0.2490 ml, 12.25 g Au in 1000 ml), $\text{Pd}(\text{NO}_3)_2$ (2 ml, 0.0054 g in 2ml) and CsNO_3 (2 ml, 0.1510 g in 2ml).

Catalyst Composition 3 - 2.5wt% Au/2.5wt% Pd/ $\text{Cs}_{2.8}\text{H}_{0.2}\text{PW}_{12}\text{O}_{40}$

A further example of a catalyst composition in accordance with the first aspect of the present invention in which the gold and palladium are provided as particles on the support of a heteropolyacid support was produced as follows. A heteropolyacid free of metal catalyst ($\text{Cs}_{2.8}\text{H}_{0.2}\text{PW}_{12}\text{O}_{40}$) was prepared by adding a solution of CsNO_3 (Aldrich) drop-wise to an aqueous solution of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (containing the appropriate amount of the acid) while stirring. The resulting solution was continuously stirred while heating at 60 °C for 12 h to obtain a solid product which was then dried overnight at 70 °C, followed by calcination at 300 °C for 2 h to form the heteropolyacid support without catalytic metal.

PdCl_2 (0.042 g, Johnson Matthey) was added to aqueous $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ solution (2.5 ml, 5g in 250 ml) and stirred at 80 °C until the palladium salt had dissolved completely. The $\text{Cs}_{2.8}\text{H}_{0.2}\text{PW}_{12}\text{O}_{40}$ was then added to the gold/palladium solution and stirred to form a paste. The paste was dried (110 °C, 16 h) before calcination (300 °C, 2 h) in static air.

Catalyst Composition 4 - $\text{Pd}_{0.325}\text{Au}_{0.217}\text{Cs}_{1.5}\text{H}_{0.2}\text{PW}_{12}\text{O}_{40}$

A further example of a catalyst composition in accordance with the present invention was made substantially as described above with reference to Catalyst Composition 1. To prepare 1 g of this catalyst composition the following aqueous solutions were used: $\text{H}_3\text{PW}_{12}\text{O}_{40}$ solution (3 ml, 0.9132 g in 3 ml), Au solution (1.7060 ml, 12.25 g Au in 1000 ml), $\text{Pd}(\text{NO}_3)_2$ (2 ml, 0.0237 g in 2ml) and CsNO_3 (2 ml, 0.0927 g in 2ml).

Catalyst Composition 5 - $\text{Au}_{0.1}\text{Cs}_{2.5}\text{H}_{0.2}\text{PW}_{12}\text{O}_{40}$

A heteropolyacid catalyst composition in accordance with the present invention comprising gold distributed throughout the catalyst composition was prepared substantially as described above with reference to Catalyst Composition 1, but without incorporating any palladium into the catalyst.

Catalyst Composition 6 - 5wt% Au/ $\text{Cs}_{2.8}\text{H}_{0.2}\text{PW}_{12}\text{O}_{40}$

A heteropolyacid catalyst composition in accordance with the present invention comprising gold deposited as particulate on the surface of a support was prepared substantially as described above with reference to Catalyst Composition 3, but without incorporating any palladium in the catalyst.

Catalyst composition 2 formed on TiO₂

50wt% Pd_{0.075}Au_{0.05} Cs_{2.5}H_{0.2}PW₁₂O₄₀/TiO₂ was prepared by first supporting the appropriate amount of CsNO₃ on to TiO₂ using incipient wetness at 80°C in open air. The paste formed was dried for 16 hours at 110°C and calcined in static air at 400°C for 4 hours to form a Cs-TiO₂ support. Appropriate amounts of H₃PW₁₂O₄₀ and Pd(NO₃)₂ were dissolved separately in deionised water. The Pd(NO₃)₂ solution, together with the appropriate amount of H₃PAuCl₄.3H₂O, was added to the H₃PW₁₂O₄₀ solution. The mixture was stirred thoroughly for 50 minutes, after which the Cs-TiO₂ support was added (with excess water). The mixture was stirred overnight at ambient temperature. Excess water was then evaporated at 70°C. The remaining solid was then dried at 110°C for 12 hours, and then calcined in static air at 300°C for 2 hours.

The manufacture or source is now described of several catalysts to be used as comparative examples, the performance of which may be compared to the performance of the examples of the catalyst compositions in accordance with the present invention.

Comparative Catalyst 1 - Cs_{2.8}H_{0.2}PW₁₂O₄₀

A heteropolyacid free of metal catalyst (Cs_{2.8}H_{0.2}PW₁₂O₄₀) was prepared by adding a solution of CsNO₃ (Aldrich) drop-wise to an aqueous solution of H₃PW₁₂O₄₀ (containing the appropriate amount of the acid) while stirring. The resulting solution was continuously stirred while heating at 60 °C for 12 h to obtain

a solid product which was then dried overnight at 70 °C, followed by calcination at 300 °C for 2 h to form the heteropolyacid catalyst without catalytic metal.

Comparative Catalyst 2 - $\text{Pd}_{0.15}\text{Cs}_{2.5}\text{H}_{0.2}\text{PW}_{12}\text{O}_{40}$

A heteropolyacid catalyst composition comprising palladium distributed throughout the catalyst composition was prepared substantially as described above with reference to Catalyst Composition 1, but without incorporating any gold into the catalyst.

Comparative catalyst 3 - 5wt% Pd/ $\text{Cs}_{2.8}\text{H}_{0.2}\text{PW}_{12}\text{O}_{40}$

A heteropolyacid catalyst composition comprising palladium deposited as particulate on the surface of a support was prepared substantially as described above with reference to Catalyst Composition 3, but without incorporating any gold in the catalyst.

Comparative catalyst 4 - 2.5wt% Au/2.5wt% Pd/Carbon support

A catalyst composition comprising gold and palladium provided as particulate on the surface of a carbon support was prepared as follows. PdCl_2 (0.042 g, Johnson Matthey) was added to aqueous $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ solution (2.5 ml, 5g in 250 ml) and stirred at 80 °C until the palladium salt had dissolved completely. Activated carbon was then added to the gold/palladium solution and stirred to form a paste. The paste was dried (110 °C, 16 h) before calcination (300 °C, 2 h).

Comparative catalyst 5 - 2.5wt% Au/2.5wt% Pd/Carbon support acidified with nitric acid

A catalyst composition comprising gold and palladium provided as particulate on the surface of a carbon support which had been treated with a solution of nitric acid, washed several times with water till the pH was neutral and then dried (such an acid treated carbon referred to as acid-washed carbon), was made as follows. The general methodology used to make Comparative Catalyst 6 was followed, but impregnation was performed on an acid-washed carbon support.

Comparative catalyst 6 - $\text{Pd}_{0.65}\text{Cs}_{1.5}\text{H}_{0.2}\text{PW}_{12}\text{O}_{40}$

A heteropolyacid catalyst composition comprising palladium distributed throughout the catalyst composition was prepared substantially as described above with reference to Catalyst Composition 1, but without incorporating any gold into the catalyst.

The ability of the catalyst compositions of the present invention to catalyse production of hydrogen peroxide from hydrogen and oxygen was investigated as follows. 10mg of each catalyst was charged into an autoclave containing the appropriate 8.5g solvent (water (2.9g)/methanol (5.6g) mixture or water only (8.5g)). The autoclave was then filled with either (i) air (4MPa, 2% hydrogen/air) or (ii) a mixture of 5% hydrogen/carbon dioxide (2.9MPa) and 25% oxygen/carbon dioxide (1.1MPa), giving a hydrogen:oxygen ratio of about 1:1.9. Stirring (1200 rpm) was started on reaching the desired reaction temperature (2°C or ambient temperature), and experiments were performed for 30 minutes. Gas analysis for

hydrogen and oxygen was performed by gas chromatography using a thermal conductivity detector. Conversion of hydrogen was calculated by gas analysis before and after reaction. Hydrogen peroxide yield was determined by titration of aliquots of the final filtered solution with acidified $\text{Ce}(\text{SO}_4)_2$ (7×10^{-3} Molar). $\text{Ce}(\text{SO}_4)_2$ solutions were standardised against $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ using ferroin as an indicator.

The results obtained for the catalyst compositions of the present invention are shown in Tables 1 and 2. Table 1 shows the data collected for experiments performed in the mixture of hydrogen and oxygen in carbon dioxide. Table 2 shows the data collected for experiments performed in the mixture of hydrogen in air.

Table 1

Catalyst	Hydrogen peroxide productivity (mol kg _{cat} ⁻¹ h ⁻¹)		
	2°C, MeOH/Water	Ambient temp. MeOH/Water	Ambient temp. Water only
Catalyst composition 1	97	107	58
Catalyst composition 2	86	178	61
Catalyst composition 2 on TiO ₂	41	58	47
Catalyst composition 3	198	30	3
Catalyst composition 4	261	228	40
Catalyst composition 5	16	35	18
Catalyst composition 6	14	34	16
Comparative catalyst 1	1	2	22
Comparative catalyst 2	96	43	27
Comparative catalyst 3	136	41	4
Comparative catalyst 4	110	98	4
Comparative catalyst 5	160	102	4
Comparative catalyst 6	144	37	13

Table 2

Catalyst	Hydrogen peroxide productivity (mol kg _{cat} ⁻¹ h ⁻¹)		
	2°C, MeOH/Water	Ambient temp. MeOH/Water	Ambient temp. Water only
Catalyst composition 1	43	49	11
Catalyst composition 2	46	48	14
Catalyst composition 3	63	57	8
Catalyst Composition 5	8	10	7
Catalyst composition 6	6	14	6
Comparative catalyst 1	0.7	8	6
Comparative catalyst 2	4	10	7
Comparative catalyst 3	61	51	7
Comparative catalyst 4	22	-	6
Comparative catalyst 5	26	-	8

The results in Tables 1 and 2 show that the catalyst compositions of the present invention, particularly those comprising gold and palladium, are particularly effective at low temperatures in a water/alcohol solvent system, using both the hydrogen in air and hydrogen/oxygen mix in carbon dioxide.

The examples of the catalyst compositions of the present invention in which the gold and palladium is distributed throughout the catalyst composition are particularly effective compared to the comparative catalysts at ambient temperatures with both water and water/alcohol catalysts, for both the hydrogen in air and the hydrogen/oxygen mix in carbon dioxide.

The example of the catalyst composition of the present invention in which the gold and palladium are provided as particulate on the surface of the heteropolyacid support was effective compared to the comparative catalysts at ambient temperature in water/alcohol for the hydrogen in air system.

It should be noted that the data for comparative catalysts 4 and 5 (gold and palladium provided as particulate on the surface of a carbon support) would not in any way suggest that the use of gold and palladium with a heteropolyacid support would prove to be effective. Furthermore, the data from the comparative catalysts in which palladium alone is distributed throughout the catalyst composition show a dramatic decrease in productivity when the temperature is raised from 2°C to ambient temperature. The catalyst compositions of the present invention comprising gold and palladium distributed throughout the catalyst composition show a highly surprising increase or only a small decrease in productivity when the temperature is raised from 2°C to ambient temperature.

A more detailed analysis of the kinetics of formation of hydrogen peroxide is shown in Figure 1. Figure 1 shows hydrogen peroxide productivity for Catalyst Composition 2 and Comparative Catalyst 4 as a function of time using a mixed water/methanol solvent at ambient temperature. The total weight of hydrogen peroxide formed is marked by the circular markers and hydrogen peroxide productivity is marked by square markers. The solid lines are used for Catalyst Composition 2

and dashed lines are used for Comparative Catalyst 4. Not only is the hydrogen peroxide productivity greater for Catalyst Composition 2 than for Comparative Catalyst 4, but the total weight of hydrogen peroxide formed is greater.

Characterisation experiments

Some of the Catalyst Compositions mentioned above were characterised using techniques well-known to those skilled in the art.

Fourier transform infrared spectroscopy

FT-IR spectra of samples were measured using a Varian Excalibur 400 spectrometer in reflection mode. Atmospheric peaks were removed using a control sample. The FTIR spectra of Catalyst Compositions 2 and 3 showed the characteristic features of a keggin structure (N. Essayem et al., Journal of Catalysis, 2001, vol. 197, pages 273-280).

Powder x-ray diffraction

X-ray diffraction (XRD) measurements were obtained from powder samples using a (θ - θ) PANalytical X'pert Pro powder diffractometer using a Cu K α radiation source operating at 40 KeV and 40mA. Samples were supported on an amorphous silicon wafer and data were obtained by scanning between 2θ values of 10-80°. Diffraction patterns of phases were identified using the International Centre for Diffraction Data (ICDD) database. XRD measurements were obtained for Catalyst Compositions 2, 4, 5 and 6, and for Comparative Catalyst 1. The XRD data for each sample showed reflections which were consistent with the cubic structure of the Cs₃PW₁₂O₄₀ salt (ICDD no. 00-051-1857). The XRD data from Catalyst Composition 4 (which has a lower Cs content) also shows peaks consistent with the presence of

$\text{H}_3\text{PW}_{12}\text{O}_{40}$. The XRD data from Catalyst Composition 6 show peaks at 2θ values consistent with the presence of metallic gold.

Temperature-programmed desorption

TPD profiles were recorded using a Thermo 1100 series TPDRO (Temperature Programmed Desorption, Reduction & Oxidation) instrument. 0.1g of sample was packed into the sample tube using quartz wool and a volume reducer. The sample was then pre-treated under helium while being heated from room temperature to 110°C at $5^\circ\text{C}/\text{min.}$, where it was held for 60mins. The sample was allowed to cool to room temperature, following which ammonia was passed over the sample for 10 minutes. The sample was then heated from room temperature to 900°C at $5^\circ\text{C}/\text{min.}$, and the ammonia desorption profile recorded using a thermal conductivity detector with positive polarity and a gain of 10.

The relative amount of ammonia uptake per g of catalyst composition was calculated, using measured ammonia uptake of $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ as a standard. $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ was prepared in a manner similar to that outlined above for Comparative Catalyst 1. Results for ammonia uptake are shown in Table 3.

Table 3

Catalyst	Relative ammonia uptake per g of catalyst
$\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$	1.00
Comparative Catalyst 2	0.81
Catalyst Composition 5	0.72
Catalyst Composition 2	1.11
Catalyst Composition 4	4.73

The TPD profiles of all the catalysts tested confirm that the catalysts have acidic character, and that the amount and strength of the acid sites depend on the caesium content and the identity of the metals incorporated into the catalyst structure. Each of the Cs_{2.5} catalysts shows a smaller ammonia desorption peak than the Cs_{1.5} catalysts. The desorption peak for the Cs_{2.5} catalysts was centred at about 800°C, whereas the desorption peak for the Cs_{1.5} catalysts was centred at about 550-570°C, indicating that the acid sites are weaker in the Cs_{1.5} catalysts than in the Cs_{2.5} catalysts.

Raman spectroscopy Raman experiments were performed using a RENISHAW inVia Raman microscope, using a 25mW power laser set at a reflection wavelength of 514nm. The laser was set to a power output of 5% in order to avoid damaging samples in the study and obtaining the best result clarity.

Raman spectra were obtained for Catalyst Compositions 1, 2 and 6, and for Comparative Catalysts 1, 2, 3 and 6. Each showed Raman bands related to atomic vibrations characteristic of peroxocomplex fragments in the range 0-1200cm⁻¹. Raman bands at 996 and 1006cm⁻¹ were observed, these being associated with $\nu(\text{W}=\text{O})$ bond vibrations while a single band at 915cm⁻¹ corresponds to the $\nu(\text{O}-\text{O})$ vibration set. A broader band observed at 550cm⁻¹ has been assigned to two possible features; specifically asymmetric and/or symmetry vibrational modes of the W-(O₂) bond. Bands located at lower frequencies (236, 216, 160, 154 and 109cm⁻¹) arise from the deformation of complex fragments in the heteropolyacid framework (Z.P. Pai et al., J. Materials Science, 2008, vol. 44, pages 541-544). Catalyst Composition 6 produced extra bands at 318 and 342cm⁻¹. Whilst not wishing to be bound by theory, it is believed that the presence of these extra bands may be attributable to the presence of the gold. It is clear from the Raman data that

each of the tested materials generates a spectrum which contains bands consistent with heteropolyacids.

A Raman spectrum was also obtained for Catalyst Composition 2 prepared on TiO_2 , the preparation of which is described above. The Raman bands shown were consistent with the presence of a heteropolyacid and TiO_2 , with two of the characteristic TiO_2 bands (395 and 518cm^{-1}) being shifted to slightly higher shift values (399 and 525cm^{-1} , respectively). Whilst not wishing to be bound by theory, it is believed that the shift to slightly higher values may be associated with an interaction between the heteropolyacid and the TiO_2 .

X-ray photoelectron spectroscopy (XPS)

XPS measurements were made on a Kratos Axis Ultra DLD spectrometer using monochromatic AlK_α radiation (source power 120 – 180 W). An analyser pass energy of 160 eV was used for survey scans, and 40 eV for detailed acquisition of individual elemental regions. Samples were mounted using double-sided adhesive tape, and binding energies referenced to the $\text{C}(1s)$ binding energy of adventitious carbon contamination taken to be 284.7 eV. Spectra were quantified using CasaXPS (Neil Fairley, UK) and surface compositions (atom %) of the sample determined. XPS measurements were made on Catalyst Compositions 1, 2, 3, 5 and 6, and on Comparative Catalysts 1, 2 and 3. The data for Catalyst Compositions 3 and 6 and for Comparative Catalyst 3 (the catalysts prepared by impregnation) show the presence of impregnated metal (Au and Pd for Catalyst Composition 3, Au for Catalyst Composition 6 and Pd for Comparative Catalyst 3) in the surface of the sample analysed. XPS data for Catalyst Compositions 1, 2 and 5 (catalysts made using the ion exchange technique) do not show the presence of catalytic metal (i.e. gold or palladium) in

the surface of the samples. Whilst not wishing to be bound by theory, it is possible that the catalytic metal is incorporated into the porous structure of the heteropolyacid support. XPS data from Comparative Catalyst 2 (containing palladium and made by the ion exchange technique) do show the presence of palladium in the surface of the sample. Those skilled in the art will realise that XPS typically only provides information on the composition of the top 1-10nm of a surface.

Where in the foregoing description, integers or elements are mentioned which have known, obvious or foreseeable equivalents, then such equivalents are herein incorporated as if individually set forth. Reference should be made to the claims for determining the true scope of the present invention, which should be construed so as to encompass any such equivalents. It will also be appreciated by the reader that integers or features of the invention that are described as preferable, advantageous, convenient or the like are optional and do not limit the scope of the independent claims.

Claims

1. A method of producing hydrogen peroxide in which hydrogen and oxygen are contacted with a catalyst composition comprising a heteropolyacid support and gold.
2. A method according to claim 1 wherein the method takes place at a temperature in the range from 0°C to 50°C.
3. A method according to claim 1 or claim 2 wherein the reaction takes place in a reaction medium and wherein the liquid component of the reaction medium is aqueous.
4. A method according to claim 3 wherein the liquid component of the reaction medium is at least 60wt% water.
5. A method according to claim 4, wherein the liquid component of the reaction medium is at least 90wt% water.
6. A method according to any preceding claim wherein the catalyst composition further comprises palladium.
7. A method according to claim 6 wherein the catalyst composition comprises at least one further catalytic metal in addition to gold and palladium.
8. A method according to claim 6 or claim 7 wherein gold and palladium are distributed throughout the catalyst composition.
9. A method according to claim 8, wherein the catalyst composition comprises from 0.1 to 5 wt% gold and palladium.
10. A method according to claim 9 wherein the catalyst composition comprises from 0.1 to 3 wt% gold and palladium.

11. A method according to claim 10 wherein the catalyst composition comprises from 0.1 to 1 wt% gold and palladium.
12. A method according to claim 6 or claim 7 wherein gold and palladium are provided as particles present on the surface of the heteropolyacid support.
13. A method according to claim 12 wherein the catalyst composition comprises from 0.5 to 10wt% gold and palladium.
14. A method according to claim 13 wherein the catalyst composition comprises from 1 to 6wt% gold and palladium.
15. A method according to claim 13 wherein the catalyst composition comprises from 3 to 5wt% gold and palladium.
16. A method according to claim 6 and any one of claims 7 to 15 when dependent on claim 6, preceding claim, wherein the molar ratio of palladium:gold is in the range of from 0.1:1 to 10:1.
17. A method according to claim 16 wherein the molar ratio of palladium:gold is in the range of from 0.2:1 to 5:1.
18. A method according to claim 16 wherein the molar ratio of palladium:gold is in the range of from 1:1 to 3:1.
19. A method of treating polluted water with hydrogen peroxide, said method comprising generating hydrogen peroxide using a catalyst composition.
20. A method according to claim 19 wherein the catalyst composition comprises one or more reactive metals.

21. A method according to claim 20 wherein the catalyst composition comprises one or more of gold, palladium, platinum, tin, ruthenium and rhodium.
22. A method according to any of claims 19 to 21, wherein the catalyst composition comprises a support.
23. A method according to claim 22 wherein the support comprise one or more of a heteropolyacid, TiO_2 , SiO_2 , CeO_2 , ZrO_2 , carbon, Al_2O_3 , Fe_2O_3 , MgO and a zeolite.
24. A method according to any of claims 19 to 23 wherein the catalyst composition comprises a heteropolyacid support and gold.
25. A method according to any of claims 19 to 24 wherein the hydrogen peroxide is generated by contacting hydrogen and oxygen with the catalyst composition.
26. A method according to any of claims 19 to 25, comprising generating hydrogen peroxide upstream of the polluted water.
27. A method according to any of claims 19 to 26 wherein hydrogen peroxide is generated in clean water, which is then admixed with the polluted water.
28. A method according to any of claims 19 to 27 wherein the temperature of the polluted water is up to 50°C .
29. A catalyst composition comprising a heteropolyacid support and gold.
30. A catalyst composition according to claim 29, wherein the catalyst composition further comprises palladium.
31. A catalyst composition according to claim 30, wherein gold and palladium are distributed throughout the

catalyst composition, and the catalyst composition comprises from 0.1 to 5 wt% gold and palladium.

32. A catalyst composition according to claim 30, wherein gold and palladium are provided as particles present on the surface of the heteropolyacid support, and the catalyst composition comprises from 0.5 to 10wt% gold and palladium.
33. A method of making a heteropolyacid catalyst composition in accordance with claims 29 to 32, said method comprising:
- (i) Generating a heteropolyacid support;
 - (ii) Depositing a gold salt onto the heteropolyacid support to form a catalyst precursor;
 - (iii) Calcining the catalyst precursor to form a heteropolyacid catalyst composition.
34. A method of making a heteropolyacid catalyst composition in accordance with claims 29 to 32, said method comprising:
- (i) Reacting a gold salt with an acid to form a catalyst precursor;
 - (ii) Calcining the catalyst precursor to form a heteropolyacid catalyst composition.

1/1

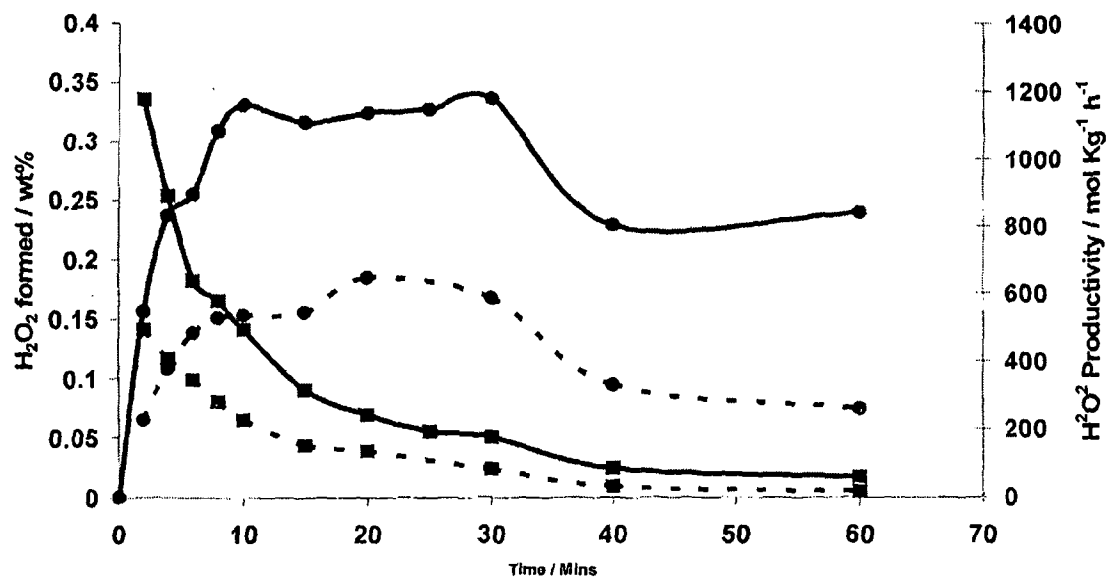


Figure 1

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2011/000377

A. CLASSIFICATION OF SUBJECT MATTER

INV. C01B15/029 B01J27/188 B01J27/186 B01J23/52
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C01B B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, CHEM ABS Data, API Data, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 1 157 739 A1 (SHOWA DENKO KK [JP]) 28 November 2001 (2001-11-28) table 1	29-32
Y	----- LI ET AL: "Direct synthesis of hydrogen peroxide from H₂ and O₂ using zeolite-supported Au-Pd catalysts", CATALYSIS TODAY, ELSEVIER, NL, vol. 122, no. 3-4, 10 May 2007 (2007-05-10), pages 361-364, XP022068755, ISSN: 0920-5861, DOI: 10.1016/J.CATTOD.2007.01.019 the whole document ----- -/--	1-18, 29-34



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

24 May 2011

Date of mailing of the international search report

18/08/2011

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Van der Poel, Wim

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2011/000377

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	PARK S ET AL: "Direct synthesis of hydrogen peroxide from hydrogen and oxygen over palladium-exchanged insoluble heteropolyacid catalysts", 10 January 2009 (2009-01-10), CATALYSIS COMMUNICATIONS, ELSEVIER SCIENCE, AMSTERDAM, NL, PAGE(S) 391 - 394, XP025691789, ISSN: 1566-7367 [retrieved on 2008-10-14] the whole document	1-18, 29-34
X	US 2002/119092 A1 (JONES C ANDREW [US] ET AL) 29 August 2002 (2002-08-29) claims	1,29
X	US 5 320 821 A (NAGASHIMA HIROMITSU [JP] ET AL) 14 June 1994 (1994-06-14) claims	1,29,33, 34
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X	US 3 433 582 A (CAMPBELL JOHN STEWART) 18 March 1969 (1969-03-18) the whole document	1,29,33, 34
X	US 6 117 409 A (BERTSCH-FRANK BIRGIT [DE] ET AL) 12 September 2000 (2000-09-12) column 4, line 1 - line 11	1,29,33, 34
X	J.K.EDWARDS ET AL.: "Direct synthesis of H ₂ O ₂ from H ₂ and O ₂ over gold, palladium, and gold-palladium catalysts supported on acid-pretreated TiO ₂ ", ANGEWANDTE CHEMIE - INTERNATIONAL EDITION 20091026 WILEY-VCH VERLAG DEU, vol. 48, no. 45, 26 October 2009 (2009-10-26), pages 8512-8515, XP002638554, DOI: DOI:10.1002/ANIE.200904115 abstract	1,29
X	EDWIN NTAIJUA N, ET AL.: "Effect of halide and acid additives on the direct synthesis of hydrogen peroxide using supported gold-palladium catalysts", CHEMSUSCHEM JUNE 2009 WILEY-VCH VERLAG DEU, vol. 2, no. 6, June 2009 (2009-06), pages 575-580, XP002638555, DOI: 10.1002/CSSC.200800257 abstract	1,29

INTERNATIONAL SEARCH REPORT

International application No.
PCT/GB2011/000377

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
1-18, 29-34

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-18, 29-34

Catalyst comprising heteropolyacid support and gold, process for making the catalyst and method for making hydrogen peroxide using the catalyst.

2. claims: 19-28

Method for treating polluted water with hydrogen peroxide, the method comprising generating hydrogen peroxide using a catalyst composition

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/GB2011/000377

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